Hydrido Platinum Metal Macrocyclic Complexes: The Synthesis and Single-crystal *X*-Ray Structure of *cis*-[IrCl(H)L^1]PF$_6$ {L^1=7-Methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene}†

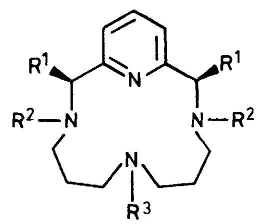
Alexander J. Blake, Timothy I. Hyde, and Martin Schröder *
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Reaction of $IrCl_3 \cdot 3H_2O$ with one equivalent of 7-methyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^1) in refluxing aqueous EtOH for 72 h affords the hydridoiridium(III) complex [IrCl(H)L^1]PF$_6$. This crystallises in the monoclinic space group $P2_1/c$, with a = 10.028(4), b = 11.926(6), c = 16.539(9) Å, β = 99.23(4)°, and Z = 4. A single-crystal *X*-ray structure shows octahedral Ir^{III} bound to the folded pyridine-2,6-diyl macrocycle L^1 [Ir–N(3) 2.080(11), Ir–N(11) 2.083(11), and Ir–N(17) 1.952(10) Å] with the fourth N donor, N(7), bent away to bind at an axial position [Ir–N(7) 2.266(11) Å]. The Ir atom lies 0.09 Å out of the triaza plane defined by N(3), N(11), and N(17). Chloro and hydrido ligands complete the octahedral co-ordination around the metal centre. The former [Ir–Cl 2.393(4) Å] lies *trans* to the pyridyl N(17) donor, with the latter *trans* to N(7); N(17)IrCl 175.7(3), HIrN(7) 172(5)°. The mechanism of formation of the complex, and the role of hydrido species as intermediates in the insertion of platinum metal ions into macrocyclic ligands, are discussed.

We have been investigating the synthesis, structure, and redox properties of platinum metal complexes of tetra-aza macrocyclic ligands.[1–3] As part of this study, we have been concerned with the metal-insertion reactions of relatively non-labile third-row transition-metal ions into macrocyclic configurations. Although the synthesis of iridium porphyrins is documented,[4–7] very few examples of iridium complexes of tetra-aza and related macrocycles have been reported.[2,8,9] Poon *et al.*[8] have prepared a series of complexes *cis*- and *trans*-[IrX$_2$(L)]$^+$ (L = 1,4,8,11-tetra-azacyclotetradecane, 1,4,8,12-tetra-azacyclopentadecane, C-*meso*- and C-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane; X = Cl, Br, or NO$_2$) by controlled addition of alcoholic solutions of L to refluxing methanolic solutions of K$_2$[IrX$_6$]. The paucity of such species reflects the difficulties encountered in the synthesis of iridium amine complexes in general, with yields of products being often low due to substitutionally inert starting materials and competing hydrolysis and redox reactions.[8,10] We therefore utilised long reflux times under relatively vigorous reaction conditions in attempts to prepare iridium(III) pyridyl macrocyclic complexes.

Results and Discussion

Reaction of $IrCl_3 \cdot 3H_2O$ with one equivalent of compound L^1 in refluxing aqueous EtOH for 72 h afforded a yellow solution from which a pale brown solid could be isolated in moderate yield (36%) on addition of NH$_4$PF$_6$. The complex was recrystallised from MeOH. In addition to bands due to co-ordinated L^1 and to PF$_6^-$ counter ion, the i.r. spectrum of the product showed bands at 2 138 and 283 cm^{-1} assigned to iridium–hydride, ν(Ir–H), and iridium–chloride, ν(Ir–Cl), stretching vibrations respectively. Iridium–hydride stretching vibrations are generally found to fall within the range 2 200—2 000 cm^{-1}.[11] The ^{1}H n.m.r. spectrum of the complex showed resonances for co-ordinated L^1, and a singlet at δ −22.25 p.p.m. assigned to a co-ordinated hydride. These data and elemental analysis results suggested a stoicheiometry of [IrCl(H)L^1]PF$_6$ for the product. Fast-atom bombardment (f.a.b.) mass spectral data were in agreement with this formulation {M^+ found = 477, calc. = 477 for [^{193}Ir^{35}Cl(H)L^1]$^+$}. For the complex [IrCl(H)L$_4$]$^+$ (L = piperidine) a *trans* geometry for the hydride and chloride ligands has been assigned on the basis of the ν(Ir–H) and ν(Ir–Cl) stretching vibrations occurring at 2 198 and 241 cm^{-1} respectively.[12] Jenkins and Shaw[13] have investigated a series of octahedral chloroiridium(III) complexes and found that the ν(Ir–Cl) occurred in the region 249—246 cm^{-1} for systems with hydride *trans* to chloride. For our macrocyclic product, [IrCl(H)L^1]$^+$, the ν(Ir–Cl) stretching vibration at 283 cm^{-1} suggested that a nitrogen donor (a donor of lower *trans* influence than hydride) was *trans* to chloride. In view of the fact that no iridium(III) tetra-aza macrocycles or hydridoiridium(III) tetra-amine complexes had been structurally characterised, and to confirm the proposed *cis* chlorohydride moiety in the product, we undertook a crystallographic study of [IrCl(H)L^1]PF$_6$. Recrystallisation of the complex from MeNO$_2$ afforded pale brown crystals suitable for a diffraction study.



L^1 R^1 = R^2 = H, R^3 = Me
L^2 R^1 = R^3 = Me, R^2 = H

The single-crystal *X*-ray structure of [IrCl(H)L^1]PF$_6$ shows octahedral iridium(III) co-ordinated to all four nitrogen donors of L^1, with the chloro and hydrido ligands bound mutually *cis* to one another. A view of the *cis*-[IrCl(H)L^1]$^+$ cation is shown in the Figure. The Ir atom is bound equatorially to three of the N donors of L^1 [Ir–N(3) 2.080(11), Ir–N(11) 2.083(11), and Ir–N(17) 1.952(10) Å] with the fourth N donor, N(7), bent away

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† *cis*-Chlorohydrido{7-methyl-3,7,11,17-tetra-azabicyclo[11.3.1]-heptadeca-1(17),13,15-triene-$N^3N^7N^{11}N^{17}$}iridium(III) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

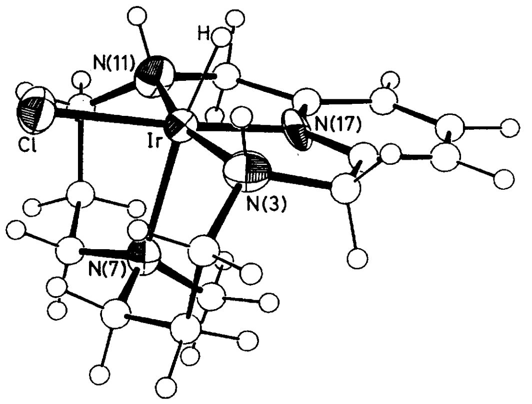

Figure. Structure of the $[IrCl(H)L^1]^+$ cation with the numbering scheme adopted

Table 1. Selected bond lengths (Å) with standard deviations for *cis*-$[IrCl(H)L^1]PF_6$

Ir–Cl	2.393(4)	C(6)–N(7)	1.485(18)
Ir–H	1.57(13)	N(7)–C(7N)	1.505(18)
Ir–N(3)	2.080(11)	N(7)–C(8)	1.487(18)
Ir–N(7)	2.266(11)	C(8)–C(9)	1.542(21)
Ir–N(11)	2.083(11)	C(9)–C(10)	1.487(23)
Ir–N(17)	1.952(10)	C(10)–N(11)	1.508(20)
C(1)–C(2)	1.512(20)	N(11)–C(12)	1.470(20)
C(1)–C(16)	1.389(20)	C(12)–C(13)	1.544(21)
C(1)–N(17)	1.324(17)	C(13)–C(14)	1.415(21)
C(2)–N(3)	1.518(18)	C(13)–N(17)	1.353(17)
N(3)–C(4)	1.509(19)	C(14)–C(15)	1.351(23)
C(4)–C(5)	1.525(22)	C(15)–C(16)	1.383(22)
C(5)–C(6)	1.523(22)		

to bind at an axial position [Ir–N(7) 2.266(11) Å]. The Ir atom lies 0.09 Å out of the triaza plane defined by N(3), N(11), and N(17) and is displaced towards the axial donor N(7). This plane makes a dihedral angle of 5.29° to the pyridyl ring, the hingeing of the pyridyl ring being towards H rather than N(7). A similar folded conformation of the tetra-aza macrocyclic ligand has been observed previously for *cis*-$[RuCl(CO)L^2]^+$.[2] The chloro and hydrido ligands complete the octahedral co-ordination around the metal centre. The chloro ligand [Ir–Cl 2.393(4) Å] lies *trans* to the pyridyl N(17) donor, with the hydride *trans* to N(7); N(17)IrCl 175.7(3), HIrN(7) 172(5)°. The iridium-bound H was located and freely refined giving a final Ir–H bond distance of 1.57(13) Å. The hydride does not participate in any significant intermolecular contacts. The intramolecular H $\cdots$ Cl distance was found to be 3.04(13) Å. The *trans* influence of the hydride ligand is illustrated by the elongation of the Ir–N(7) bond length by approximately 0.14 Å. A similar *trans* influence is observed in the cation $[RhH(NH_3)_5]^{2+}$ in which an increase of 0.165 Å is noted[14] in the Rh–N bond length *trans* to the hydride in comparison to the *cis* Rh–N bond lengths.

The stability of $[IrCl(H)L^1]^+$ is of interest. Although many stable iridium(III) hydrido complexes are known, most utilise one or more π-acceptor ligands in their stabilisation.[15] Stable hydrido amine complexes of Rh^{III} have been prepared,[14] but only one example of a hydrido tetra-amine complex, $[IrCl(H)L_4]^+$ (L = piperidine), has been reported.[12] Poon *et al.*[8] have postulated the intermediacy of hydrido species in the synthesis of complexes of Rh^{III}, Ir^{III}, Ru^{III}, and Os^{III} of tetra-aza macrocycles in alcoholic media. The mechanism of formation of the cation $[IrCl(H)L^1]^+$ is unclear, although reduction of inert Ir^{III} by the alcoholic solvent to give a labile iridium(I) intermediate, which inserts into the macrocyclic ligand, appears likely. Subsequent formal oxidative addition of HCl to '$[IrL^1]^+$' (in a *cis* manner) would afford the isolable, stable iridium(III) hydrido species *cis*-$[IrCl(H)L^1]^+$. The iridium(III) ion has an ionic radius of 0.68 Å[16] and is therefore sufficiently small to be accommodated by the pyridyl ligand in an equatorial configuration; the synthesis of *trans* products of Ir^{III} and Rh^{III} is being investigated.

Table 2. Selected bond angles (°) with standard deviations for *cis*-$[IrCl(H)L^1]PF_6$

Cl–Ir–H	98(5)	C(5)–C(6)–N(7)	114.1(12)
Cl–Ir–N(3)	97.2(3)	Ir–N(7)–C(6)	110.7(8)
Cl–Ir–N(7)	89.0(3)	Ir–N(7)–C(7N)	113.8(8)
Cl–Ir–N(11)	97.4(3)	Ir–N(7)–C(8)	110.5(8)
Cl–Ir–N(17)	175.7(3)	C(6)–N(7)–C(7N)	109.2(10)
H–Ir–N(3)	83(5)	C(6)–N(7)–C(8)	104.8(10)
H–Ir–N(7)	172(5)	C(7N)–N(7)–C(8)	107.3(10)
H–Ir–N(11)	90(5)	N(7)–C(8)–C(9)	116.2(12)
H–Ir–N(17)	78(5)	C(8)–C(9)–C(10)	116.9(13)
N(3)–Ir–N(7)	93.2(4)	C(9)–C(10)–N(11)	113.4(13)
N(3)–Ir–N(11)	164.5(4)	Ir–N(11)–C(10)	118.4(9)
N(3)–Ir–N(17)	82.2(4)	Ir–N(11)–C(12)	111.4(9)
N(7)–Ir–N(11)	92.4(4)	C(10)–N(11)–C(12)	111.8(11)
N(7)–Ir–N(17)	95.3(4)	N(11)–C(12)–C(13)	112.0(12)
N(11)–Ir–N(17)	82.8(4)	C(12)–C(13)–C(14)	125.4(13)
C(2)–C(1)–C(16)	122.8(13)	C(12)–C(13)–N(17)	114.9(12)
C(2)–C(1)–N(17)	115.8(12)	C(14)–C(13)–N(17)	119.7(13)
C(16)–C(1)–N(17)	121.4(13)	C(13)–C(14)–C(15)	117.5(14)
C(1)–C(2)–N(3)	111.4(11)	C(14)–C(15)–C(16)	122.8(15)
Ir–N(3)–C(2)	110.4(8)	C(1)–C(16)–C(15)	117.1(14)
Ir–N(3)–C(4)	117.3(8)	Ir–N(17)–C(1)	119.8(9)
C(2)–N(3)–C(4)	111.4(10)	Ir–N(17)–C(13)	118.6(9)
N(3)–C(4)–C(5)	113.4(12)	C(1)–N(17)–C(13)	121.5(11)
C(4)–C(5)–C(6)	116.5(13)		

Table 3. Selected torsion angles (°) with standard deviations

C(16)–C(1)–C(2)–N(3)	173.3(13)
N(17)–C(1)–C(2)–N(3)	−5.9(17)
C(2)–C(1)–C(16)–C(15)	−179.0(14)
N(17)–C(1)–C(16)–C(15)	0.1(21)
C(2)–C(1)–N(17)–C(13)	178.8(12)
C(16)–C(1)–N(17)–C(13)	−0.4(20)
C(1)–C(2)–N(3)–C(4)	138.8(12)
C(2)–N(3)–C(4)–C(5)	−73.5(15)
N(3)–C(4)–C(5)–C(6)	−68.9(17)
C(4)–C(5)–C(6)–N(7)	74.2(17)
C(5)–C(6)–N(7)–C(7N)	67.6(15)
C(5)–C(6)–N(7)–C(8)	−177.7(12)
C(6)–N(7)–C(8)–C(9)	176.2(12)
C(7N)–N(7)–C(8)–C(9)	−67.8(15)
N(7)–C(8)–C(9)–C(10)	−71.6(17)
C(8)–C(9)–C(10)–N(11)	66.6(18)
C(9)–C(10)–N(11)–C(12)	75.2(16)
C(10)–N(11)–C(12)–C(13)	−140.9(13)
N(11)–C(12)–C(13)–C(14)	−174.5(14)
N(11)–C(12)–C(13)–N(17)	6.6(18)
C(12)–C(13)–C(14)–C(15)	−178.8(15)
N(17)–C(13)–C(14)–C(15)	0.1(22)
C(12)–C(13)–N(17)–C(1)	179.3(12)
C(14)–C(13)–N(17)–C(1)	0.3(20)
C(13)–C(14)–C(15)–C(16)	−0.3(24)
C(14)–C(15)–C(16)–C(1)	0.2(24)

Iridium hydrido complexes of porphyrins have recently been shown to be useful catalytic precursors. Thus, the use of iridium hydrido porphyrin complexes [Ir(oep)H] (H_2oep = 2,3,7,8,12,

Table 4. Fractional co-ordinates of atoms with standard deviations

Atom	*x*	*y*	*z*
Ir	0.315 68(5)	0.521 37(4)	0.380 82(3)
Cl	0.524 6(3)	0.438 0(3)	0.360 00(21)
H	0.304(13)	0.465(11)	0.465(8)
C(1)	0.148 9(13)	0.674 4(12)	0.451 8(8)
C(2)	0.286 6(14)	0.725 5(12)	0.479 5(9)
N(3)	0.397 9(10)	0.653 1(9)	0.454 9(7)
C(4)	0.504 7(15)	0.723 3(13)	0.424 4(9)
C(5)	0.458 8(16)	0.772 5(14)	0.339 4(10)
C(6)	0.437 8(15)	0.689 8(12)	0.268 3(9)
N(7)	0.313 6(11)	0.620 8(9)	0.263 8(7)
C(7N)	0.191 7(14)	0.695 1(12)	0.242 6(9)
C(8)	0.316 8(14)	0.544 2(13)	0.193 2(9)
C(9)	0.202 8(15)	0.456 4(13)	0.177 4(10)
C(10)	0.208 3(17)	0.362 4(14)	0.236 9(10)
N(11)	0.187 6(11)	0.399 1(9)	0.321 2(7)
C(12)	0.045 2(15)	0.425 2(14)	0.324 2(10)
C(13)	0.030 1(13)	0.528 7(13)	0.378 1(8)
C(14)	−0.093 0(15)	0.569 1(14)	0.398 5(9)
C(15)	−0.087 9(17)	0.662 3(14)	0.445 4(10)
C(16)	0.031 4(15)	0.718 1(13)	0.473 7(9)
N(17)	0.146 7(10)	0.583 5(10)	0.405 7(5)
P(1)	0.773 3(4)	0.571 9(4)	0.108 9(3)
F(1)	0.871(7)	0.627(4)	0.183(3)
F(2)	0.701(4)	0.687 7(21)	0.092(3)
F(3)	0.760(6)	0.667(7)	0.050(6)
F(4)	0.763(7)	0.569(7)	0.020 1(17)
F(5)	0.845(5)	0.455(4)	0.122(4)
F(6)	0.668(5)	0.505(3)	0.052(4)
F(7)	0.892(5)	0.559(5)	0.055(4)
F(8)	0.631(3)	0.526(4)	0.102(4)
F(9)	0.897(3)	0.641(3)	0.136(3)
F(10)	0.829(5)	0.465(4)	0.148(3)
F(11)	0.675(6)	0.632(11)	0.145(6)
F(12)	0.747(7)	0.563(6)	0.198 3(25)

13,17,18-octaethylporphyrin) in the four-electron reduction of O_2 (*via* the formation of [{Ir(oep)}$_2$] dimer)[5] and in the synthesis of iridium formyl complexes[6] has been described. The insertion of the [{Ir(oep)}$_2$] dimer into C–H bonds to afford alkyl and hydrido species has also been reported.[7] The ability of L^1 to function in a similar manner to the above porphyrin ligand is however limited due to the involvement of competing ligand oxidative dehydrogenation reactions. Products isolated after standing at ambient temperature for several days in solution showed that decomposition of $[IrCl(H)L^1]^+$ had occurred. The i.r. spectrum of the new product shows loss of both the ν(Ir–H) and amine, ν(N–H), stretching vibrations at 2 138 and 3 151 cm^{-1} respectively, with the appearance of new bands in the region 1 600—1 550 cm^{-1} assigned to imine, ν(C=N), stretching vibrations. Further evidence for this was obtained from the ^1H n.m.r. spectrum which showed no signal in the hydride region, but new resonances at δ 8.9—9.0 tentatively assigned to macrocyclic methine protons. This suggests that oxidative dehydrogenation of the C–N linkages has occurred in solution to afford mono-and di-iminopyridyl products. Insertion of Rh and Ir into peralkylated macrocycles in order to arrest this decomposition route is in progress.

Experimental

Infrared spectra were measured as Nujol mulls, KBr and CsI discs using a Perkin-Elmer 598 spectrometer over the range 200—4 000 cm^{-1}. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. Fast-atom bombardment mass spectra (using a glycerol–dimethylformamide solvent matrix) and electron-impact (e.i.) mass spectra were run on a Kratos MS 50TC spectrometer. Proton and ^{13}C n.m.r. spectra were obtained on Bruker WP200 and WP80 instruments.

Synthesis of Compound L^1.—The free ligand L^1 was prepared using the methods developed by Busch and Karn[17] (Found: C, 66.7; H, 9.8; N, 22.1. Calc. for $C_{14}H_{24}N_4$: C, 66.7; H, 9.7; N, 22.6%). ^1H N.m.r. ($CDCl_3$, 293 K, 80 MHz): δ 7.49 (t, py, 1 H, J = 7.6), 6.95 (d, py, 2 H, J = 7.6 Hz), 3.82 (s, $C_5H_3CH_2N$, 4 H), 2.90 (br s, NH, 2 H), 2.50 (t, 4 H, J = 5.7), 2.33 (t, 4 H, J = 5.8 Hz), 2.01 (s, NCH_3, 3 H), and 1.68 (m, 4 H, $NCH_2CH_2CH_2N$). ^{13}C DEPT, N.m.r. ($CDCl_3$, 293 K, 50.32 MHz): δ 136.2, 120.3, 56.1, 54.2, 46.5, 40.7, 26.9 p.p.m. (excluding quaternary carbon resonances). Mass spectrum (e.i.): M^+ at *m/e* 248 (calc. for $C_{14}H_{24}N_4$ 248). M.p. 82—85 °C.

Synthesis of $[IrCl(H)L^1]PF_6$.—The salt $IrCl_3 \cdot 3H_2O$ (0.138 g, 0.39 mmol) and L^1 (0.082 g, 0.33 mmol) were refluxed in a mixture of ethanol (120 cm^3) and water (80 cm^3) for 72 h under N_2. After filtration and removal of 150 cm^3 of solvent, excess NH_4PF_6 was added to the clear yellow solution to give a pale brown solid. The product was collected, recrystallised from methanol, and dried *in vacuo*. Yield 75 mg, 36% {Found: C, 25.5; H, 3.9; N, 8.4. Calc. for $[IrCl(H)L^1]PF_6$: C, 25.6; H, 3.7; N, 8.5%}. ^1H N.m.r. (CD_3NO_2, 293 K, 200 MHz): δ 7.83 (t, py, 1 H), 7.32 (d, py, 2 H), 6.51 (br, NH), 4.63 (m, CH_2, 4 H), 3.33—2.5 (m, CH_2, 12 H), 2.36 (s, CH_3, 3 H), and −22.25 p.p.m. (s, IrH). Infrared spectrum (KBr disc): 3 151, 3 140, 2 138, 1 609, 1 591, and 283 cm^{-1}. Mass spectrum (f.a.b.): M^+ at *m/e* 477, 476, and 438 {calc. 477 for $[^{193}Ir^{35}Cl(H)L^1]^+$, 476 for $[^{193}Ir^{35}Cl(L^1)]^+$, and 438 for $[^{193}IrL^1 - 3\ H]^+$}.

X-*Ray Structure Determination of* $[IrCl(H)L^1]PF_6$.—A pale brown crystal (0.35 × 0.12 × 0.10 mm) suitable for *X*-ray analysis was obtained by slow evaporation of a nitromethane solution.

Crystal data. $C_{14}H_{25}ClIrN_4{}^+PF_6{}^-$, M = 622.0, monoclinic, space group $P2_1/c$, a = 10.028(4), b = 11.926(6), c = 16.539(9) Å, β = 99.23(4)°, U = 1 952 Å^3 (by least-squares refinement on diffractometer angles for 30 reflections), Z = 4, D_c = 2.116 g cm^{-3}, $\bar{\lambda}$(Mo-K_α) = 0.710 69 Å, μ = 70.93 cm^{-1}.

Data collection and processing. Stoe-Siemens AED2 four-circle diffractometer, ω—θ scans with ω scan width (0.80 + 0.35 tanθ)°, acquisition times of 25—140 s per reflection, graphite-monochromated Mo-K_α radiation; 2 915 reflections measured ($2\theta_{max.}$ = 45°, $\pm h,k,l$) in 61 h, initial absorption correction using Ψ scans giving 1 548 with amplitudes $F \geqslant 6\sigma(F)$.

Structure analysis and refinement. Patterson synthesis (Ir) followed by iterative rounds of least-squares refinement and difference Fourier synthesis[18] located all non-H atoms. At isotropic convergence, final correction for absorption was made using DIFABS.[19] Anisotropic thermal parameters were refined for Ir, N, Cl, P, and F, and methylene H atoms were included in fixed, calculated positions:[18] the iridium-bound H atom was located and refined freely. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,639F^2$ gave satisfactory analyses. At convergence, R,R' = 0.0305 and 0.0385 respectively for 231 parameters, S = 1.222. The maximum and minimum residues in the final ΔF syntheses were 1.10 and −0.98 e Å^{-3} respectively. Illustrations were prepared using ORTEP,[20] molecular geometry calculations utilised CALC,[21] and scattering factor data were taken from ref. 22. Bond lengths, angles, selected torsion angles, and fractional co-ordinates are given in Tables 1—4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining torsion angles.

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